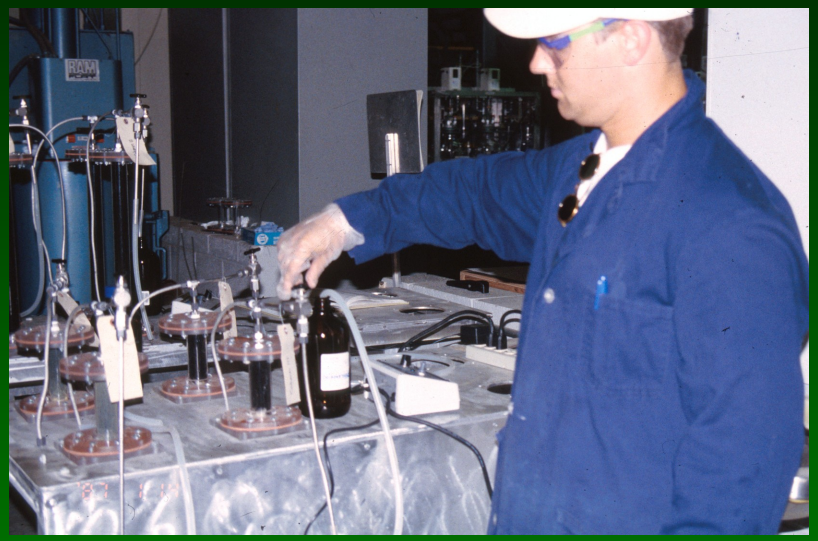
Integration of Zero-Valent Iron Reduction and Oxidation Processes for Remediation of Explosives Contamination in Groundwater



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Problem

Basic Reactions involved in ZVI Reduction

- Anaerobic corrosion
- Aerobic corrosion
- Dechlorination
- Nitro Reduction

Reduction of Nitroaromatics

three steps, each involving a two-electron reduction, with Fe^0 as the ultimate electron donor

$$ArNO_2 + Fe^0 + 2H^+ \rightarrow ArNO + Fe^{2+} + H_2O$$

$$ArNO + Fe^0 + 2H^+ \rightarrow ArNOH + Fe^{2+}$$

$$ArNHOH + Fe^0 + 2H^+ \rightarrow ArNH_2 + Fe^{2+} + H_2O$$

ZVI Process Effects

- Nitroaromatics reduced to corresponding amines and other intermediates
- Transformation products are strongly sorbed on the iron surface

Effectiveness of ZVI

- Particle size of Iron
- Metal pretreatment
- Metal to substrate ratio
- Substrate structure

(Continued)

Effectiveness of ZVI

(Concluded)

- Reaction pH
- Presence of other dissolved substances
- Exposure time
- Homogeneity of soil samples
- Whether reactions are carried out under oxic or anoxic conditions

Important Consideration

- Quantity of available surface area - reactions occur through mass transfer of contaminants to the metal surface

Previous Research

- ZVI of nitroaromatics by Agrawal and Tratnyek - nitrosobenzene → aniline
- Numerous studies of chlorinated solvents
- Hundal research

Dark Advanced Oxidation Processes

- Fenton’s reagent
- Potassium Permanganate

Fenton's Process

$$H_2O_2 + Fe^{2+} \rightarrow OH^- + OH^\bullet + Fe^{3+}$$

$$RH + OH^\bullet \rightarrow ROH + H^+$$

$$RH + OH^\bullet \rightarrow R^\bullet + H_2O$$

Objectives

- Determine ZVI reduction rate constants and capacity for TNT and RDX in pure solutions
- Determine the effects of ZVI interferences
- Assess effects of ZVI surface area
- Assess ZVI kinetics in batch and dynamic systems
- Determine efficiency of Fenton’s reagent and potassium permanganate for oxidation of TNT and RDX in pure and binary solutions
- Assess integration of oxidation / reduction systems
- Apply information from laboratory simulated solutions to desorbed waters from site soils

Materials and Methods

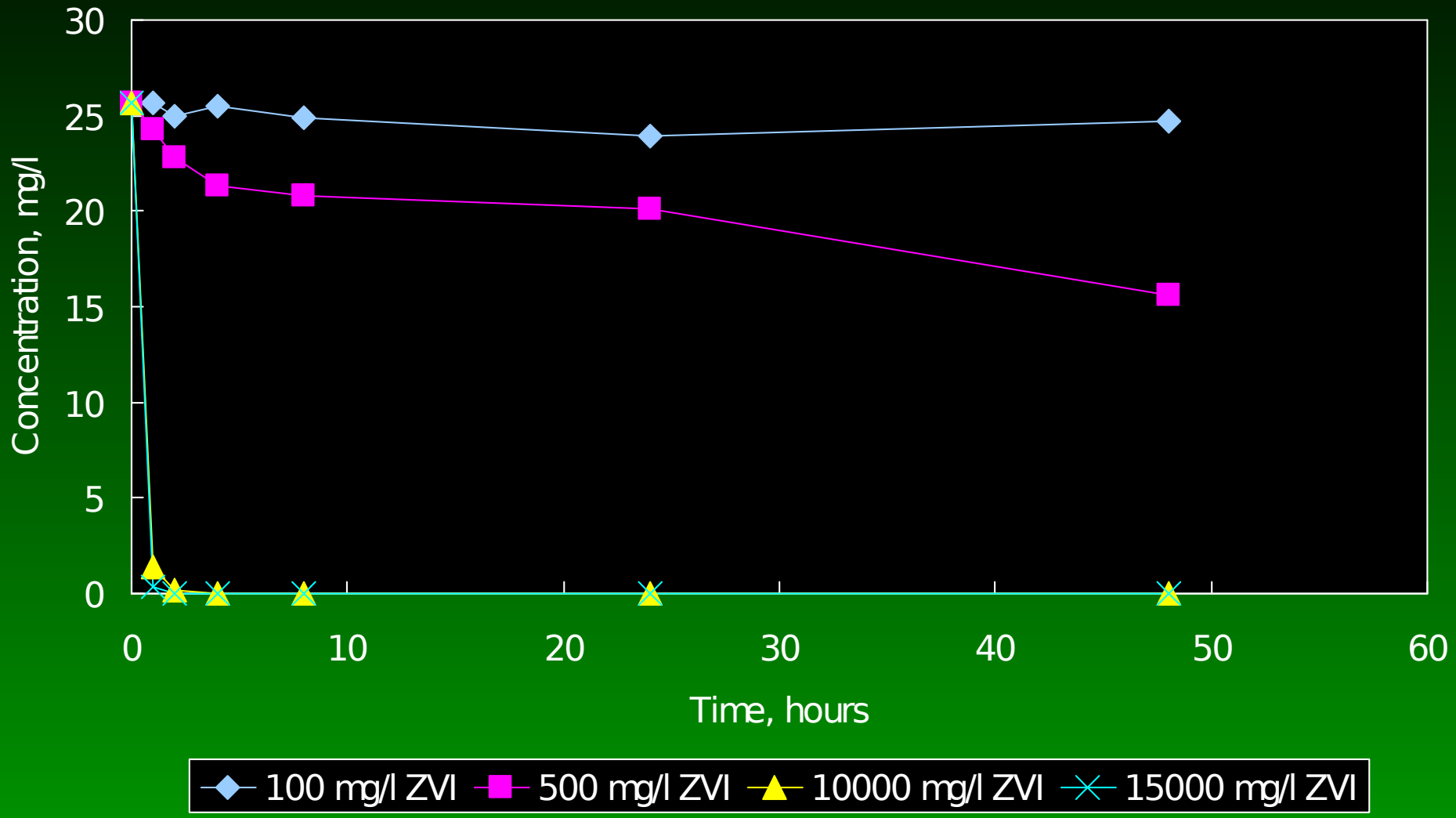
- 40 mesh iron powder
- 50% hydrogen peroxide
- Ferrous sulfate
- Potassium permanganat

Approach

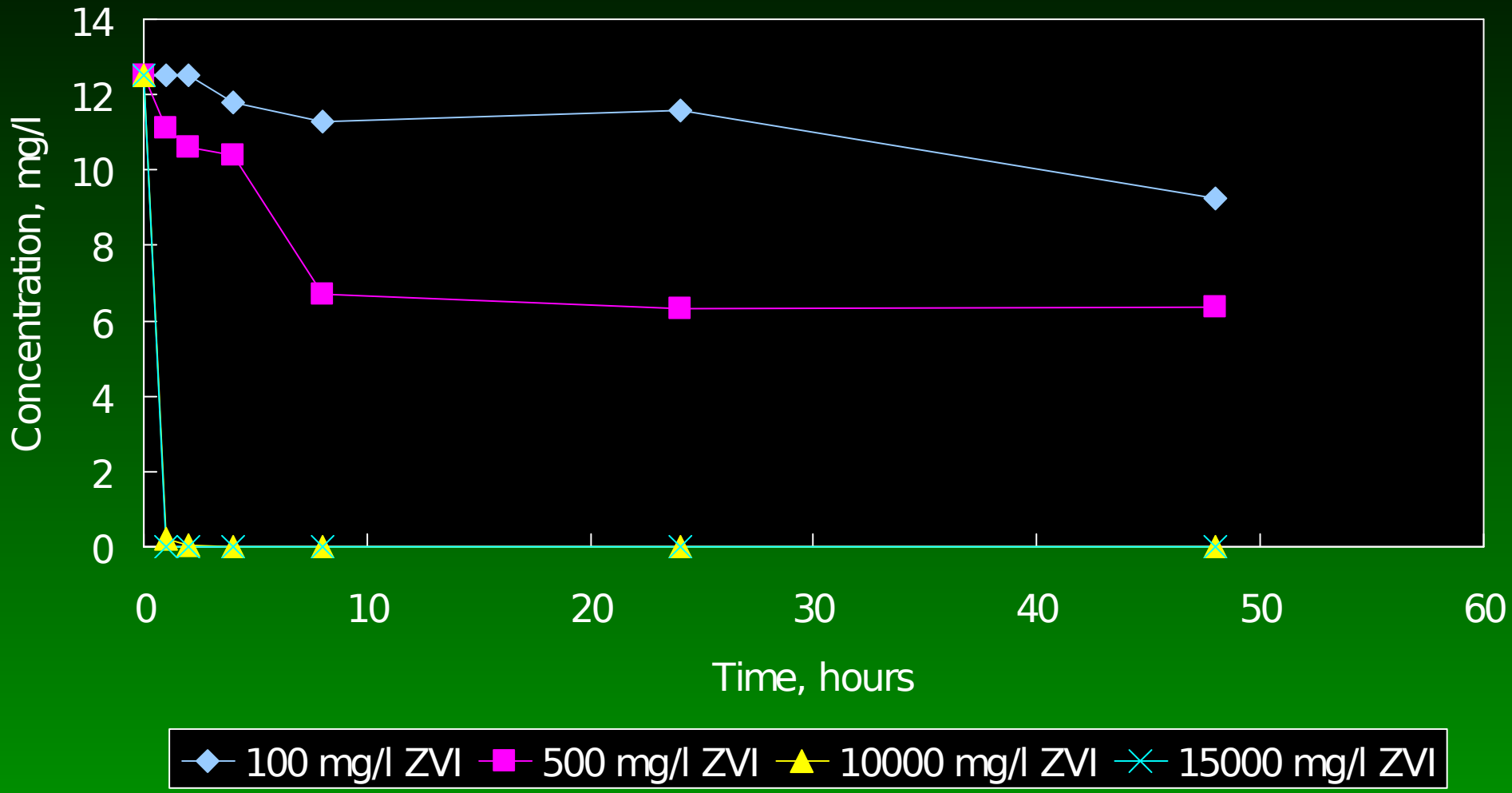
Assess the following:

- Kinetics and endproducts of ZVI Reduction of TNT and RDX
- Reduction capacity of ZVI for TNT and RDX in pure solutions
- ZVI Reduction Interferences
- Kinetics and endproducts of oxidation of TNT and RDX using Dark AOPs (Fenton’s reagent and potassium permanganate)
- Application to site waters
- Effects of multiple explosives

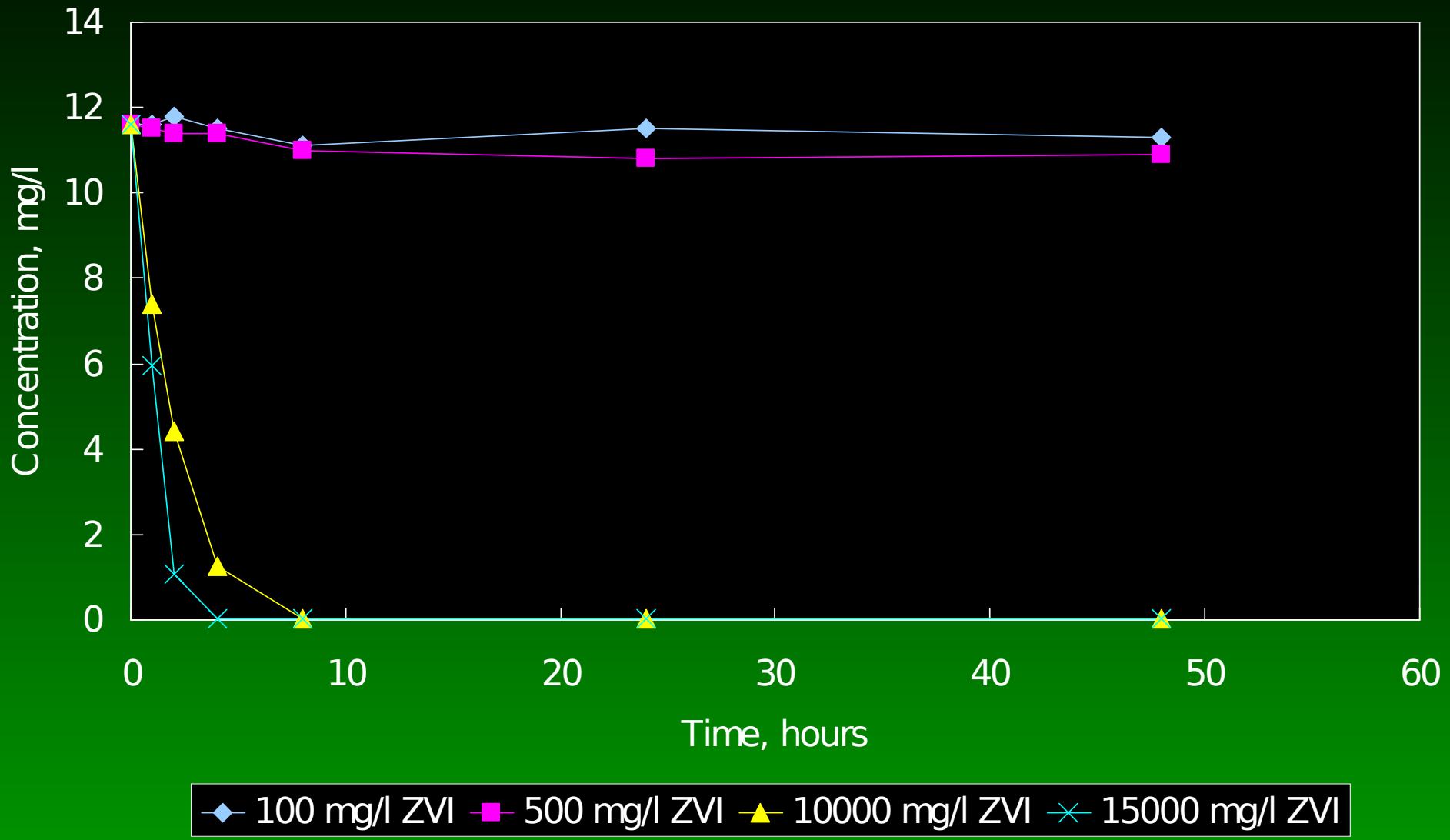
TNT Reduction, Mixed, Anaerobic



TNT (TNT & RDX), Mixed, Anaerobic



RDX (TNT & RDX), Mixed, Anaerobic



TNT Only, Anaerobic, Mixed, 10,000 mg/l ZVI

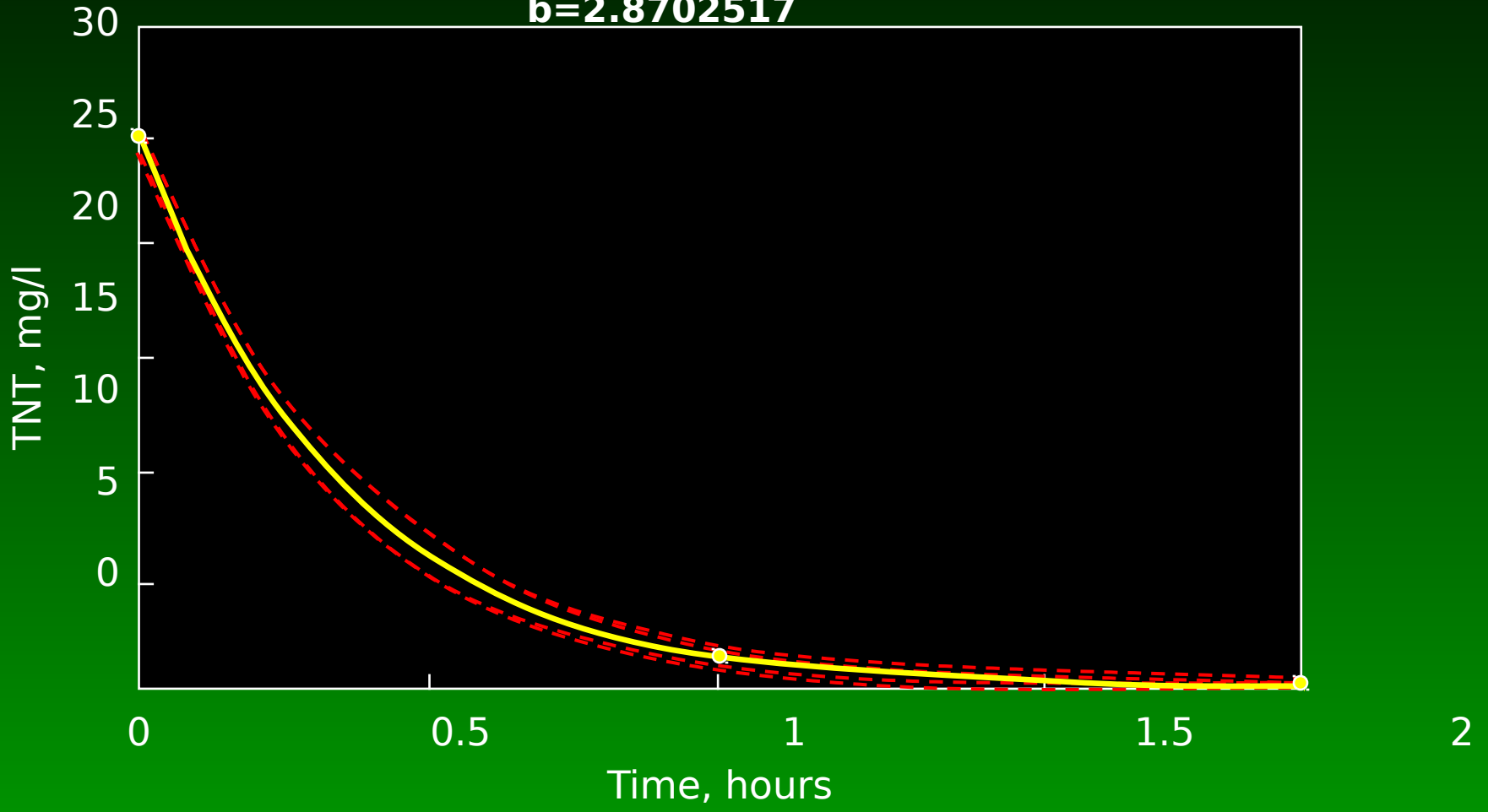
Rank 1 Eqn 8098 [Decay1_] y=aexp(-bx)

r^2=0.99998985 DF Adj r^2=0.9999797 FitStdErr=0.063073666

Fstat=98530.834

a=24.999799

b=2.8702517



RDX Only, Anaerobic, 15000 mg/l

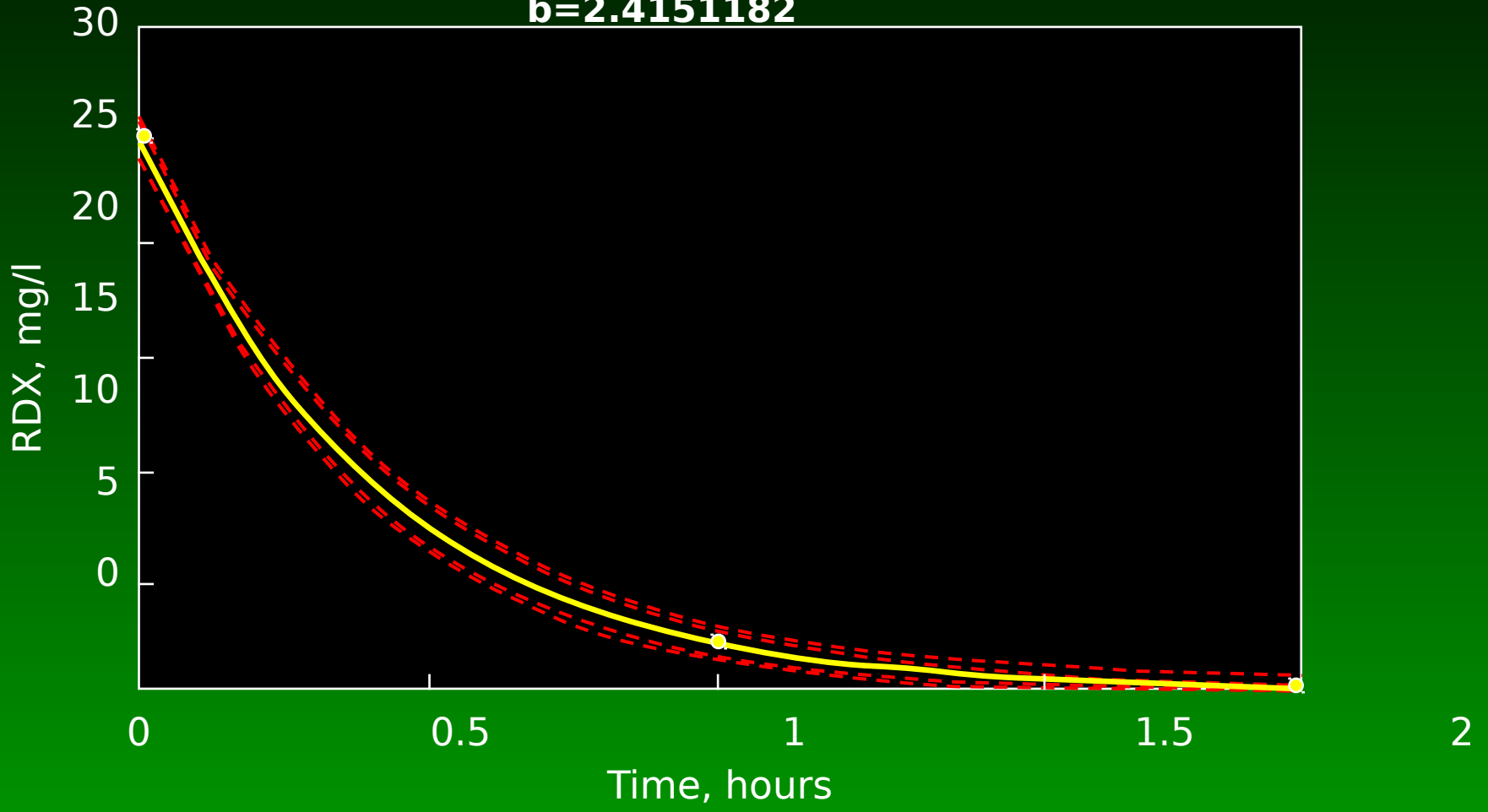
Rank 1 Eqn 8098 [Decay1_] y=aexp(-bx)

r^2=0.99997822 DF Adj r^2=0.99995644 FitStdErr=0.091044316

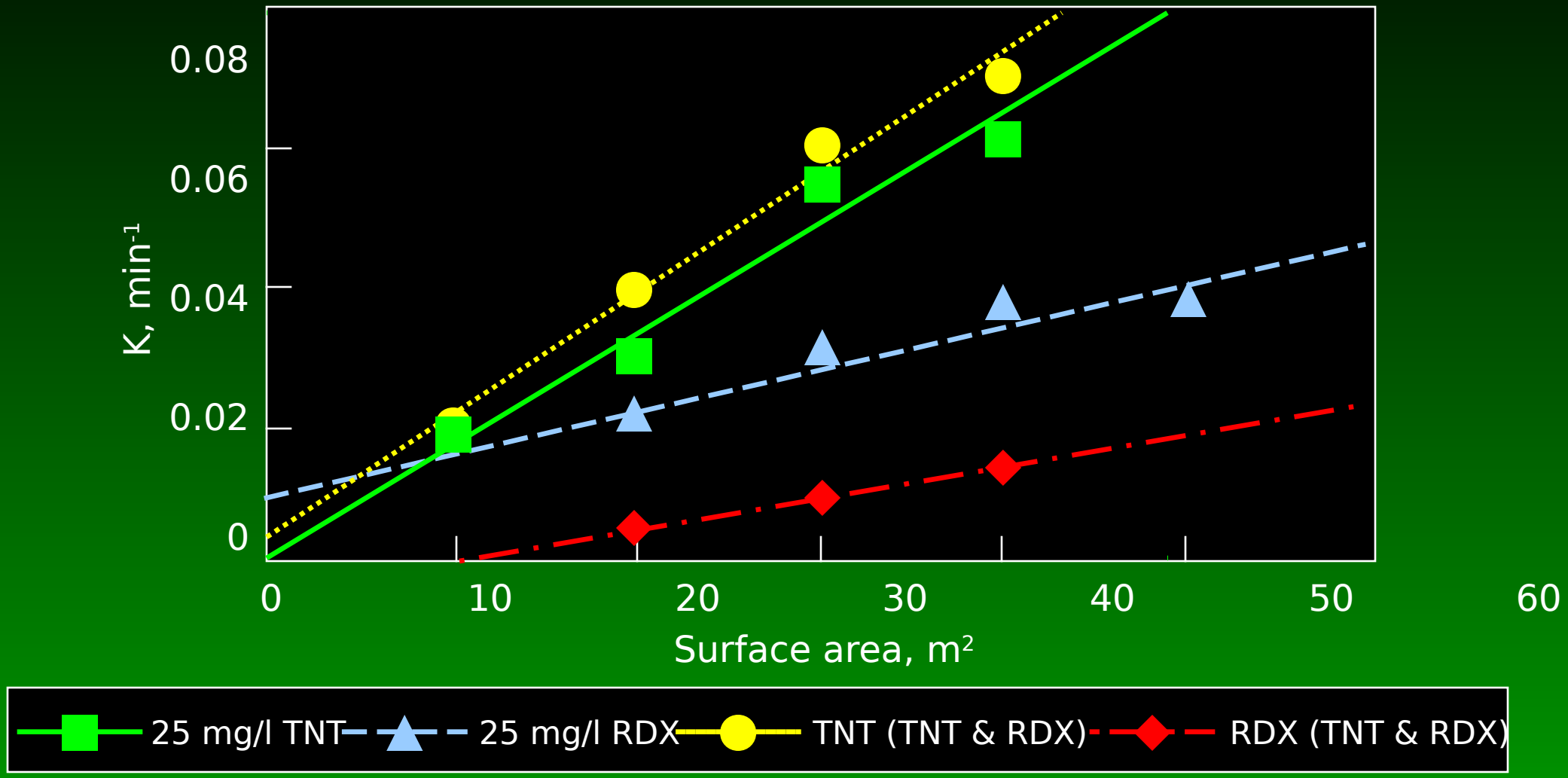
Fstat=45909.038

a=25.000716

b=2.4151182

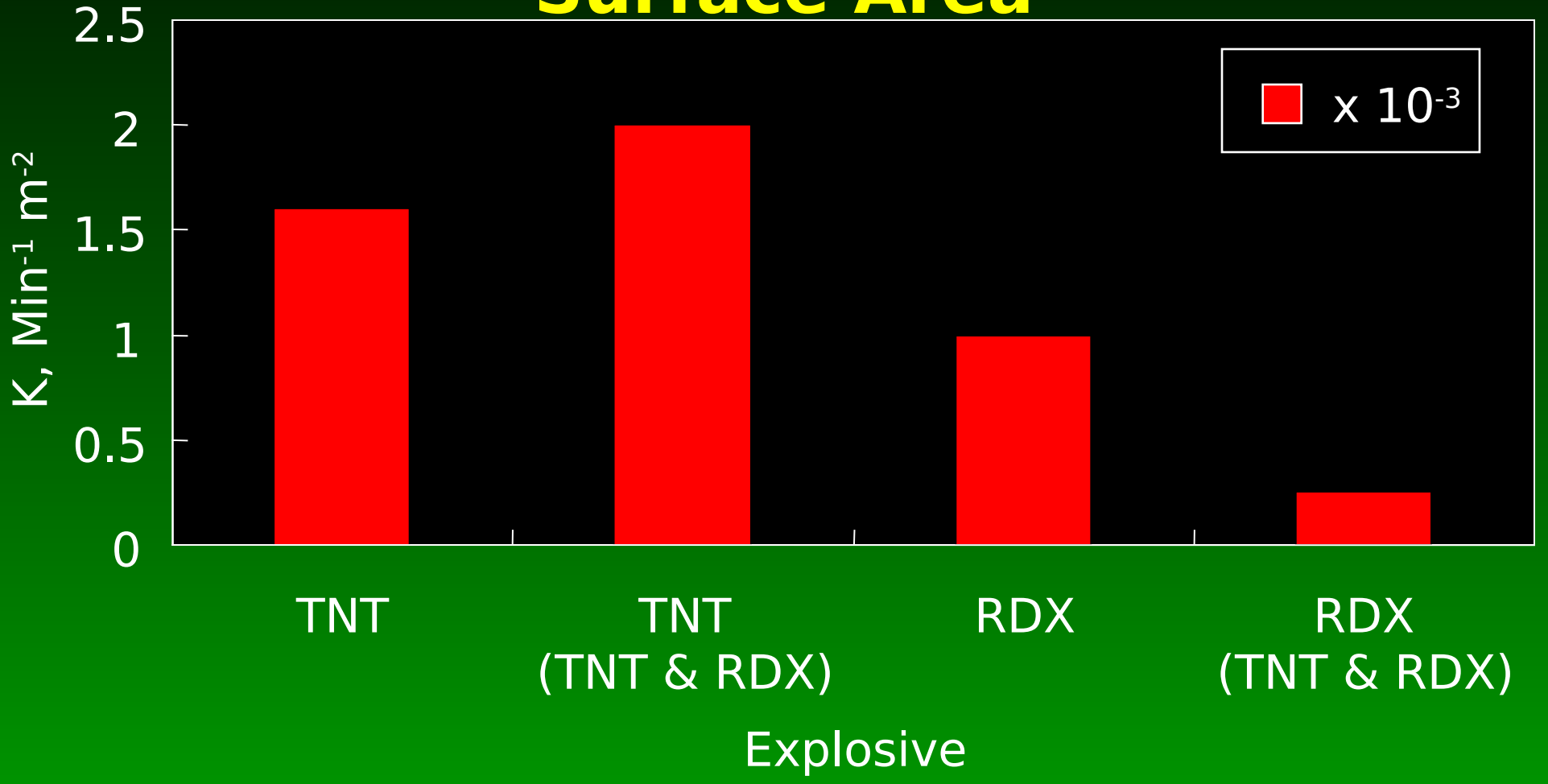


K (min^{-1}) vs. ZVI Surface Area



Results of k (min^{-1}) per Square Meter of ZVI

Surface Area



Results of Kinetic Assessments of Pure and Mixed Solutions

Explosive	Conc., mg/l	Dosage	K, min^{-1} m^{-2}	r-squared
TNT	25	5000	1.63×10^{-3}	0.993
	25	10000	2.39×10^{-3}	0.99999
	25	10000	1.49×10^{-3}	0.989
	25	20000	1.537×10^{-3}	0.979
	25	80000 *	1.16×10^{-5}	0.9835
RDX	25	10000	1.00×10^{-3}	0.972
	25	10000	1.05×10^{-3}	0.973
	25	10000	1.33×10^{-3}	0.99996
	25	15000	1.005×10^{-3}	0.942
	25	15000	1.34×10^{-3}	0.99998
	25	25000	0.737×10^{-3}	0.985
	25	20000	0.921×10^{-3}	0.96
	25	80000	1.28×10^{-5}	0.992
TNT (TNT & RDX)	12.5	5000	1.91×10^{-3}	0.992
		10000	2.01×10^{-3}	0.993
		15000	2.02×10^{-3}	0.998
		20000	1.75×10^{-3}	0.996
RDX (TNT & RDX)	12.5	10000	4.45×10^{-4}	0.999
		10000	2.23×10^{-4}	0.939
		15000	5.02×10^{-4}	0.913
		20000	3.37×10^{-4}	0.89
		80000 *	1.18×10^{-5}	0.957

* Not Mixed

esults of Fenton's Reagent and Potassium Permanganate Oxidation of TNT and RDX (Mixed

Treatment	Explosive	Dosage, mg/l	Time, hours	TNT, mg/l	TNB, mg/l	HMX, mg/l	RDX, mg/l
Fenton's	TNT Only		0	27			
			24	<0.02	0.192		
	RDX Only		0			1.0	23.0
			24			0.057	0.313
	TNT & RDX		0	12.5		0.5	12.5
			24	<0.02		0.101	0.034
Potassium Permanganate	TNT Only	0	0	27			
		1000	One week	0.256			
		1500	One week	<0.02			
	RDX Only	0	0				23.0
		1000	48				18.5
	TNT & RDX	0	0	12.5			12.5
		1000	One week	0.074			8.8

Effects of Multicomponent Explosives

Approach

- Characterization of soils
  - Percent sand, silt, clay
  - Soils pH
  - TOC content
  - CEC
  - Crystalline and amorphous
  - Aluminum oxide

Results of ZVI Reduction of filtrate from 10% Slurry of Yorktown Naval Weapons Station Soils

Yorktown Dilution	ZVI Conc	TNT, mg/l	TNB, mg/l	HMX, mg/l	RDX, mg/l
NA	NA	49.7	0.559	1.250	1.900
	500	0.059	<0.02	0.732	0.466
	500	0.140	<0.02	0.793	0.662
NA	NA	50.1	0.548	1.27	1.92
	750	<0.02	<0.02	0.587	0.069
	1000	<0.02	<0.02	0.550	0.045
	2000	<0.02	<0.02	<0.02	<0.02
	4000	<0.02	<0.02	<0.02	<0.02
1:3	NA	12.5	0.132	0.337	0.445
	750	<0.02	<0.02	0.140	0.016 J
	1000	<0.02	<0.02	0.118	0.036
	2000	<0.02	<0.02	0.106	<0.02
	4000	<0.02	<0.02	0.060	<0.02
1:10	NA	4.530	0.051	0.116	0.154
	500	0.033	<0.02	0.101	0.099
	750	<0.02	<0.02	0.077	0.046
	1000	<0.02	<0.02	0.075	0.042
	1500	<0.02	<0.02	0.078	0.042

Results of Fenton's Reagent Treatment of Filtrate from YNWS

Treatment	Time, hours	TNT, mg/l	TNB, mg/l	HMX, mg/l	RDX, mg/l
Fenton's	0	56.90	0.341	1.35	1.78
	24	<0.02	0.234	<0.02	<0.02

Conclusions

- TNT and RDX in pure solutions can be treated to below the analytical detection limit or 0.02 mg/l for TNT and RDX
- Reduction kinetics can be modeled according to pseudo-first-order reduction rate equations
- Normalized reduction rates constants for TNT and RDX in pure solutions were 1.6 x 10^{-3} min^{-1} m^{-2} and 1 x 10^{-3} m^{-2}, respectively
- The effect of binary solution assessments on TNT were to increase the pseudo-first-order-rate coefficients from approximately 1.6 x 10^{-3} min^{-1} m^{-2} to 2 x 10^{-3} min-1 m^{-2}
- The effect of binary solution assessments on RDX were to decrease the pseudo-first-order-rate coefficients from approximately 1 x 10^{-3} min^{-1} m^{-2} to 0.25 x 10^{-3} min^{-1} m^{-2}
- Non-mixed conditions reduce reduction rate constants by approximately two orders of magnitude for pure and binary solutions
- Pseudo-first-order-rate reduction rate constants in YNWS simulated waters appear to be higher than rate constants in the pure solutions for TNT and RDX. Further studies are currently being conducted
- Fenton's reagent and potassium permanganate can effectively oxidize TNT and RDX. RDX is the more recalcitrant explosive in the permanganate system